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Visible light driven photocatalyst of vanadium (V^{3+}) doped TiO_2 synthesized using sonochemical method

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Abstract. TiO_2 has been widely investigated due to its superior photocatalytic activity under ultraviolet irradiation among the photocatalyst materials. In this research, vanadium (V^{3+}) was doped into TiO_2 to enhance its light response under visible irradiation for wider application. Vanadium was introduced into TiO_2 lattice at various concentration respectively 0.3, 0.5, 0.7 and 0.9% using simple and fast sonochemical method. X-Ray Diffraction data show that vanadium doped TiO_2 crystallized in anatase phase with $I4_1amd$ space group. X-Ray Diffraction pattern shifted to lower value of 2θ due to vanadium dopant. It indicated that V^{3+} was incorporated into anatase lattice. UV-Vis Diffuse Reflectance Spectra was revealed that the doped TiO_2 has lowered reflectance and enhanced absorption coefficient in visible region than undoped TiO_2 and commercial anatase TiO_2 . Band gap energy for undoped and doped TiO_2 were respectively 3.22, 3.05, 2.93, 3.03 and 2.40 eV. Therefore vanadium doped TiO_2 had potential to be applied under visible light.

1. Introduction

Modification anatase TiO_2 with various metal dopants have been reported as one of strategy to enhance its optical absorption and photocatalytic activity under visible irradiation. Vanadium dopant has produced a higher optical absorption and lower band gap energy than Ce, Cr, Fe, and Ni dopant [1-3] thus vanadium is an attractive dopant to be studied. Vanadium in anatase lattice shown the urbach tail phenomenon [4] therefore resulted in decreasing the band gap energy and enhancing the absorption of anatase in visible light. Vanadium also affected on the phase transformation of anatase TiO_2 since vanadium has the low solubility in anatase phase (about 5 at %) [5]. Low level of vanadium (0.3%) does not induced the phase transformation and only leads a small shift in absorption edge through solid state synthesis [6]. However, 0.3% of vanadium was reported to induce the phase transformation from anatase into rutile [3] while sol gel method was employed. It can be concluded that the structural transformation and the band gap reduction can be influenced by concentration of vanadium and the synthesis method employed in photocatalyst's production.

Sonochemical method is fast and simple method which nowadays developed in synthesis of semiconductor materials. Ultrasound wave can assisted the chemical reaction and resulted in smaller particle size, homogenous particle distribution, high surface area and high purity of material. Irradiation of ultrasound wave into solution given an acoustic cavitation which is produced through bubble formation, bubble growth and collapsing the bubbles in liquids [7]. Acoustic cavitation provide an extremely high temperature and pressure in short duration to facilitate the chemical reaction on



synthesis process. Sonochemical method has been applied in synthesis of TiO_2 nanoparticle [8], Pt, Ru doped TiO_2 [9] and V doped TiO_2 1-5 at % [10]. No sufficient work reported to produce low content of vanadium doped TiO_2 using sonochemical method, therefore it became important to explore this efficient method on synthesis of vanadium doped TiO_2 . Sonochemical method at low frequency was applied in this research to study the effect of vanadium concentration (0.3-0.9 at %) on structure and optical characteristics of anatase TiO_2 .

2. Experimental

Titanium isopropoxide (TTIP, sigma Aldrich) was dissolved into 40 mL ethanol:deionize water (3:1v/v). Stoichiometric amount of vanadium acetylacetonate ($\text{V}(\text{acac})_3$, sigma aldrich) in 20 mL ethanol: deionize water (3:1v/v) added into titanium solution at 0.3, 0.5, 0.7 and 0.9% atomic ratio of vanadium III (V^{3+}). The homogenous mixture transferred into ultrasonic bath reactor and irradiated with low frequency ultrasound wave 40 KHz for 40 minutes. The obtained precipitates aged, filtered and washed with ethanol then dried at 105°C for 2h. The dry powders subsequently pressed into pellet and calcined for 2h at 500°C . Undoped TiO_2 was also synthesized using the same method with the absence of vanadium. The white powder produced for undoped TiO_2 and pale brown to brown for vanadium doped TiO_2 corresponding with increasing the vanadium concentration. The structure of synthesized materials were studied by Powder of X-Ray Diffracton (XRD). The optical properties were characterized by UV-Vis Diffuse Refflectance Spectroscopy (UV-Vis DRS). For further information, the synthesized materials also compared with commercially anatase TiO_2 purchased from Sigma Aldrich, $\geq 99\%$ purity (TiO_2 SA No.248576) without further purification.

3. Result and Discussion

XRD pattern in figure 1 shows that all synthesized materials have agreement with commercially anatase TiO_2 Sigma Aldrich (TiO_2 SA). Introducing vanadium (III) at 0.3 to 0.9% into TiO_2 lattice using sonochemical method resulted in the pure phase of anatase and does not induced the phase transformation from anatase into rutile or brukite. Further insight on XRD pattern at highest intensity peak shows that V^{3+} doped TiO_2 shifted to lower value of 2θ compared to undoped TiO_2 . The shift of 2θ attributed to alteration of d spacing material caused by specific vanadium content. It was indicated that vanadium was doped in TiO_2 lattice.

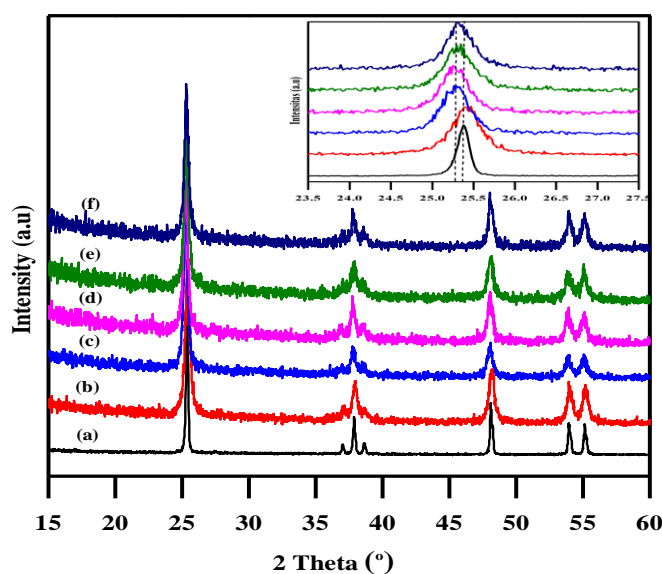


Figure 1. XRD Pattern for (a) TiO_2 SA (b) undoped TiO_2 and V^{3+} doped TiO_2 at (c) 0.3% (d) 0.5% (e) 0.7% and (f) 0.9%.

Compared to commercially TiO_2 SA, the XRD pattern of undoped and V^{3+} doped TiO_2 have broadened peaks which indicated smaller particle size. Table 1 shows the average crystallite size were calculated by Scherrer's equation at the highest intensity peak (101 plane). Average crystallite size of undoped and doped TiO_2 (0.3-0.7%) were smaller than TiO_2 SA (53.19 nm) while 0.9% of V^{3+} was larger than TiO_2 SA. Further XRD data analysis using Le Bail refinement method with anatase standart (JCPDS No. 21-1272) revealed that all materials crystallized in tetragonal lattice with $I4_1amd$ space group and 4 asymmetric unit (Z). Unit cell parameter (a, c) and unit cell volume of V^{3+} doped TiO_2 observed to decrease than undoped TiO_2 . It can be affected by different size ion between Ti^{4+} and V^{3+} . Vanadium was known as multivalence ion with different ionic radii as different oxidation state. At six coordination number, V^{3+} (0.78Å) is larger than Ti^{4+} (0.74Å) while V^{4+} (0.72Å) and V^{5+} (0.68Å) is smaller ionic radii than Ti^{4+} [4]. Substitution Ti^{4+} ion with larger V^{3+} ion can result in increasing the unit cell and crystal volume. However, decreasing the unit cell and crystal volume in this research indicating that vanadium might be present at higher valence or mixed valence in TiO_2 lattice. The larger decrease was obtained at 0.7% of Vanadium than another concentration.

Table 1. Unit Cell, Cell Volume and Average Crystallite size of undoped and doped TiO_2 .

	Undoped TiO_2	$\text{TiO}_2\text{-V}$ 0.3%	$\text{TiO}_2\text{-V}$ 0.5%	$\text{TiO}_2\text{-V}$ 0.7%	$\text{TiO}_2\text{-V}$ 0.9%
a,b (Å)	3.803	3.786	3.792	3.784	3.786
c (Å)	9.559	9.515	9.526	9.509	9.514
V (Å³)	138.217	136.414	136.990	136.195	136.419
Cryst. (nm)	34.28	34.18	26.42	26.43	79.40

UV-Vis DRS data in figure 2 shows the reduced reflectance for all vanadium doped TiO_2 materials compared to undoped TiO_2 and commercial TiO_2 SA at visible wavelength (400-800 nm). Reflectance tend to continuous decrease as increasing V^{3+} concentration and therefore the enhancement of absorption coefficient (F(R)) in inset figure was obtained. The reduced reflectance and enhanced absorption coefficient in visible wavelength indicated that vanadium doped TiO_2 which synthesized by sonochemical method had potential to be applied under visible irradiation.

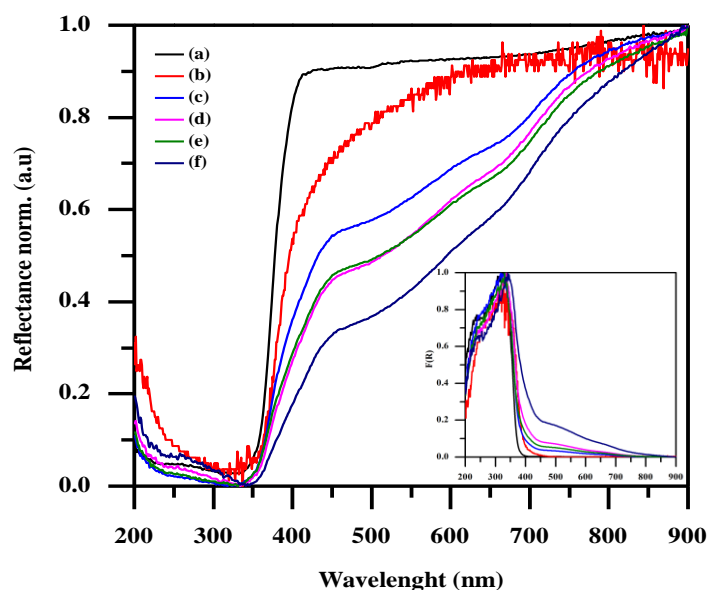


Figure 2. UV-Vis DRS data of (a) TiO_2 SA (b) undoped TiO_2 and V^{3+} doped TiO_2 at (c) 0.3% (d) 0.5% (e) 0.7% and (f) 0.9%.

Determination of bandgap energy by Kubelka-Munk transformation shown in figure 3. The bandgap energy for TiO₂ SA, undoped TiO₂ and V doped TiO₂ 0.3%, 0.5%, 0.7% , 0.9% were respectively 3.25, 3.22, 3.05, 2.93, 3.03 and 2.40 eV. The energy tend to decrease as increasing vanadium content with the highest reduction achieved at 0.9% vanadium. 0.7% of V doped TiO₂ shows slightly alteration from the trend, respecting to the refinement result which showed the largest shrinkage in unit cell parameter. This evidence may contributed by the nature of vanadium state in TiO₂ lattice at 0.7%. Furthermore, substitution of Ti⁴⁺ by vanadium at different oxidation states and different concentration may result in various spin states, oxygen vacancy, and reduction level of band gap energy as the effect of compensation method in substitutional [11] or interstitial doping.

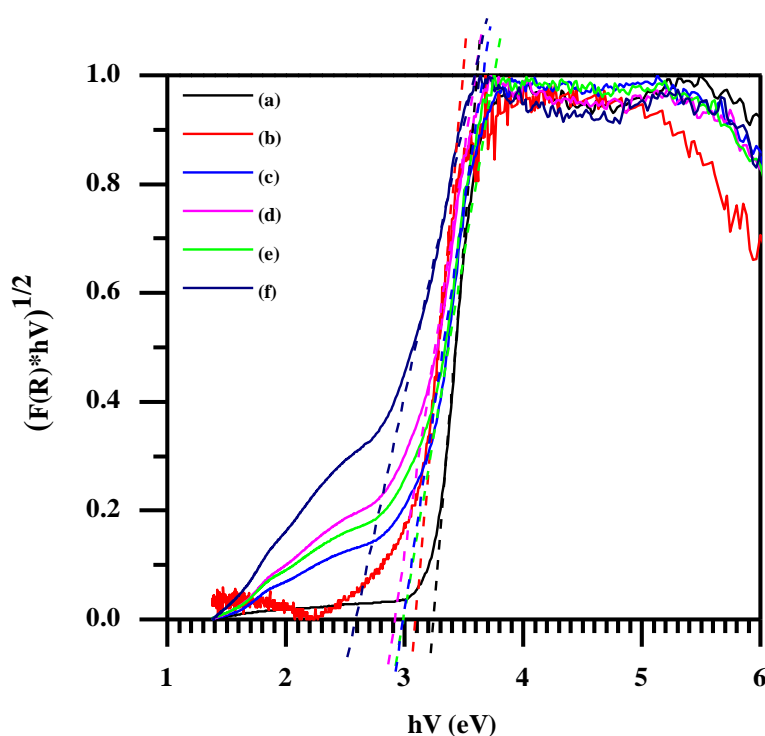


Figure 3. Bandgap energy of (a) TiO₂ SA (b) undoped TiO₂ and V³⁺ doped TiO₂ at (c) 0.3% (d) 0.5% (e) 0.7% and (f) 0.9%.

4. Conclusion

Vanadium doped TiO₂ was successfully synthesized using sonochemical method. Photocatalyst materials crystallized in pure anatase structure with tetragonal lattice and *I41amd* space group. Lower shifted of 2θ and decreased unit cell parameter indicated that anatase structure distorted due to vanadium dopant. Vanadium doped TiO₂ shows decreased bandgap energy, lowered reflectance and enhanced absorption in visible light. As a result, it had potential photocatalytic activity under visible irradiation (400-800 nm)

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